Differences in Chemical and Sensory Properties of Orange Flower and Rose Oils Obtained from Hydrodistillation and from Supercritical CO_2 Extraction

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Bitter orange flower oil, or neroli oil, and rose oil are highly valued essential oils in perfumery. Both oils are used in alcoholic perfumery, as extrait perfumes, toilet waters, after-shaves and eau de colognes. Thorough studies and excellent reviews have appeared about bitter orange flower oil and rose oil.

Kaiser and Lamparsky[1] published detailed results on the constituents of bitter orange flower headspace and the flower absolute. They could detect only 2-methylbutyronitrile in the complex mixture from the flower headspace, from which they collected a very small quantity. Several new benzenoid, monoterpenoid and sesquiterpenoid nitrogen derivatives were found in the absolute. More recent investigations of the composition and olfactive quality of bitter orange flower oil have been published by Boelens[2,3] and Anonis.[4] Lawrence[5] wrote a valuable review about the chemical composition of bitter orange oil.

Kovats[6] reported on an intensive study that was carried out on rose oil over a ten-year period in cooperation with scientists at Firmenich.[7] The study resulted in the identification of an additional 127 constituents in the oil. More recently, Lawrence[8] wrote a thorough review on the chemical composition of rose oils from different species and various origins covering 68 publications. In 1992, Brunke et al.[9] published their results of the headspace analyses of four rose cultivars of *Rosa damascena*. Ohloff[10] very recently reviewed the chemical composition of rose oil and discussed the sensory properties of the main constituents in detail. In 1991, Moates and Reynolds[13] published their studies on the extraction of rose petals using the techniques of solvent extraction (hexane), steam distillation and high-pressure carbon dioxide.

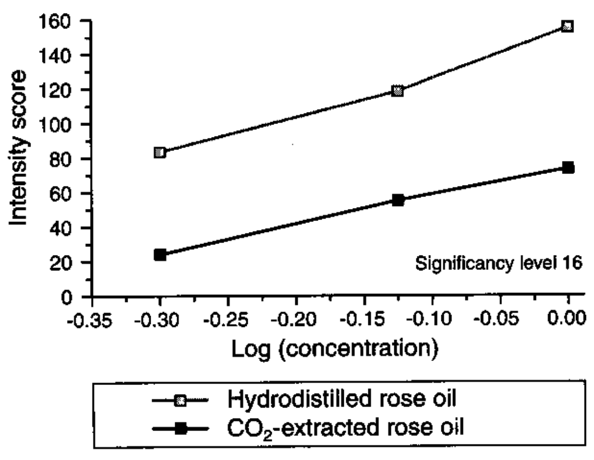

Figure 1. Intensity camparison test between rose oils.

In a recent paper, Degraff[14] focused on correlations between organoleptic characteristics and variation in component analysis in current (1990-1994) Bulgarian and Turkish rose oil samples, plus samples from older vintages for which gas chromatographic and written organoleptic comparisons were available. Her evaluation indicated that significant changes had taken place in the sensory and biological character of *R. damascena* within the 20th century.

Compounds occurring in essential oils can be classed as characteristic, essential, balance compounds or artifacts.

- Characteristic compounds are recognized by experts as representing a great deal of the olfactive quality of the oil.
- Essential compounds are necessary for the sensory quality but not for the characteristic odor quality.
- Balance compounds are neither characteristic nor essential to the aroma of an oil; they constitute the remainder of the naturally occurring materials in the oil.
- Artifacts are compounds that do not occur in the original natural material. They are, for instance, compounds formed during processing or derived from solvents, herbicides or fungicides.

In this article we will identify some characteristic and essential constituents of bitter orange flowers (*Citrus aurantium* L., ssp. *amara* Engl.) from Spain, Tunisia and Morocco, and roses (*Rosa damascena* Mill.) from Bulgaria and Turkey, and we will discuss how the consitutents differ depending on whether the oils were isolated by hydrodistillation or by supercritical fluid carbon dioxide extraction of the concretes.

Table I. Chemical composition (%) of bitter orange flower oils

Compound	Spain hydro-distilled	Tunisia hydro-distilled	Morocco CO_2 extract
α-thujene	0.01-0.05	+	+
α-pinene	0.75-1.13	0.99	0.46
camphene	0.05-0.08	0.07	0.04
sabinene	1.40-2.80	1.17	1.10
β-pinene	10.52-13.00	14.56	8.79
myrcene	1.40-3.09	2.08	1.11
α-terpinene	0.18-0.48	0.10	0.04
p-cymene	0.01-0.05	0.12	0.04
limonene	12.88-17.89	12.20	11.50
(Z)-β-ocimene	0.10-0.43	0.73	0.40
(E)-β-ocimene	5.60-7.00	6.24	4.54
γ-terpinene	0.01-0.51	0.18	0.06
terpinolene	0.42-0.60	0.42	0.16
hexyl acetate	0.01-0.05	0.05	0.04
cis-linalool oxide (5)	0.01-0.07	0.16	0.22
trans-linalool oxide (5)	0.10-0.20	0.06	0.16
linalool	31.37-47.05	37.87	34.60
2-phenylethanol	0.06-0.25	-	0.64
terpinen-4-ol	0.31-1.32	0.39	0.14
α-terpineol	1.07-3.45	4.11	1.13
nerol	0.32-0.82	0.88	0.23
neral	0.01-0.03	0.03	-
geraniol	0.80-2.28	2.00	0.40
linalyl acetate	0.58-10.00	3.30	23.60
2-phenethyl acetate	-	0.03	0.18
geranial	0.05-0.10	0.06	-
α-terpinyl acetate	0.01-0.30	0.14	0.14
neryl acetate	0.29-1.55	1.53	0.79
geranyl acetate	0.70-2.95	2.94	1.17
cis-jasmone	0.01-0.05	0.02	0.15
(Z)-methyl jasmonate	0.01	0.01	0.03
phenylacetonitrile	-	-	0.67
indole	0.10-0.16	0.16	0.45
methyl anthranilate	0.10-0.22	0.09	0.98
β-caryophyllene	0.54-0.70	0.73	0.07
(E)-β-farnesene	0.05-0.10	0.17	-
α-humulene	0.06-0.15	0.10	-
(E,E)-α-farnesene	0.05-0.10	0.11	-
γ-elemene	0.01-0.02	0.12	-
δ-cadinene	0.01-0.03	0.03	-
(E)-nerolidol	2.15-3.37	3.36	1.21
(E,Z)-farnesol	0.72-1.59	1.57	0.44
(E,Z)-farnesyl acetate	0.01-0.05	0.09	0.06

- = absent; + = present

Supercritical Fluid Carbon Dioxide Extraction

The supercritical carbon dioxide extraction of the concretes was carried out according to a method described by Reverchon et al.[11] Supercritical carbon dioxide extraction is, in principle, a simple process and is able to produce extracts for food, pharmaceutical and cosmetic use. The product is generally considered to be organoleptically superior to oils produced by traditional techniques, such as hydrodistillation. For these reasons, this technique has attracted the attention of many researchers, as reported by Moyler et al.[12]

One of the most studied problems in supercritical carbon dioxide extraction is determining optimum conditions for extraction of characteristic compounds from herbs, flowers, roots and seeds. The fluid carbon dioxide extraction plant usually adopted consists of a pressurized vessel and a single separation stage to isolate the extract by depressurizing the supercritical solution. Often this procedure is not sufficient to obtain the desired product. Moreover, to obtain the essential oils by supercritical carbon dioxide extraction, it is necessary to operate at maximum selectivity to avoid coextraction of undesired compounds. In addition, cuticular waxes have to be eliminated from the extraction.

Experimental

Supercritical carbon dioxide extraction of flower concretes was carried out by the Italian company Essences Technicals in cooperation with the Department of Chemical and Food Engineering of the University of Salerno.[11] The apparatus consists of an extractor with an internal volume of 20 l. It was charged with 1,500 g of flower concrete that was thoroughly mixed with ⅔ mm diameter glass beads. This procedure maximizes the surface contact between solute and solvent. The solution at the exit of the extractor was passed through three separators in series that were operated under conditions suitable for fractionating the extract.

GC analyses were carried out using a Carlo Erba MEGA HRGC 5300, equipped with a fused-silica column 50 m x 0.32 mm i.d. coated with SE 54 (Hewlett Packard HP-5; high performance cross linked 5% phenyl silicone gum phase), film thickness 1.05 micron. The oven temperature program was 40°-280°C at 4°C/minute; injector and FID

Table II. Concentrations (%) of main constituents in hydrodistilled and CO_2-extracted orange flower oils

Compound	Hydrodistilled oil	CO_2-extracted oils
monoterpene hydrocarbons	38	28
linalyl acetate	3-5	24
linalool	38	35
nitrogen derivatives	<0.5	2
sesquiterpene alcohols	4	<2

at 220°C; carrier gas helium, 120 kPa head pressure; inlet split 50 ml/minute.

GC/MS data were obtained on a Finnigan TSQ70 mass spectrometer directly coupled with a Hewlett Packard 5890 gas chromatograph using the same column and conditions as described above.

Results from Bitter Orange Flower Oil

Table I shows the chemical composition of the various bitter orange flower oils. No significant differences were found in the chemical composition of the hydrodistillation oils from Spain and Tunisia. The chemical composition of the CO_2-extracted oil from Moroccan bitter orange flower concrete is quite different from the compositions of the two hydrodistilled oils (Table II).

Compared to the hydrodistilled oils shown in Table II, the CO_2-extracted oil contained only three-quarters as many monoterpene hydrocarbons, up to eight times as much linalyl acetate, more than four times as many nitrogen derivatives and less than half the amount of sesquiterpene alcohols. The differences in the concentrations of the monoterpene hydrocarbons and of linalyl acetate can be explained by the fact that at least 20% of the linalyl acetate decomposed into monoterpene hydrocarbons and other monoterpenoids during the hydrodistillation. The higher concentration of the nitrogen derivatives in the carbon dioxide extract may be due to the water solubility of these compounds; they tend to remain in the water during hydrodistillation.

The odor value, quality and intensity of hydrodistilled and CO_2-extracted bitter orange flower oils were determined by a group of five perfumers. The oils were evaluated as such, and also in 1% and 0.1% solutions. The perfumers preferred the carbon dioxide extract over the hydrodistilled oil. The odor intensity of the carbon dioxide extract from the orange blossom concrete was about twice that of the hydrodistilled oils.

Results from Rose Oils

Table III shows the chemical composition of the various rose oils. The essential and characteristic constituents of the rose oils were found to be citronellol, geraniol, nerol, 2-phenylethanol, rosefuran, the rose oxides, nerol oxide, eugenol, methyl eugenol and the damasc(en)ones. The sensory properties of these compounds have been discussed in detail by Ohloff.[10,16] Moreover, Ohloff reviewed the odor units (defined as a constituent's concentration divided by its odor threshold) of the 14 main constituents of Bulgarian rose oil. Using Ohloff's method, we analyzed the Bulgarian rose oils and found the concentrations, thresholds and odor units shown in Table IV.

Clearly β-damascenone, the rose oxides and citronellol have the greatest impact on the overall olfactive quality of the oils. The total number of odor units in hydrodistilled oil was about three times that of the carbon dioxide extract.

What appears strange in the CO_2-extracted products is the amount of 2-phenylethanol: at about 67.5%, it is more than 30 times the amount found in the hydrodistilled oils. An explanation of the low 2-phenylethanol content in the hydrodistilled oils may be that the bulk of this product is lost by its solubility in the distilled water.

The odor value, quality and intensity of the hydrodistilled oil and the CO_2-extracted Bulgarian rose oils was determined by five perfumers. The oils were evaluated as such, and also in 1% and 0.1% solutions. The perfumers preferred the hydrodistilled oil over the CO_2-extracted oil. Because of this olfactive difference, the market value of

Table III. Chemical composition (%) of rose oils

Compound	Bulgaria hydro-distilled	Turkey hydro distilled	Bulgaria CO_2 extract	Compound	Bulgaria hydro-distilled	Turkey hydro distilled	Bulgaria CO_2 extract
α-pinene	0.60-0.80	0.60	0.73	2-phenethyl acetate	0.20-0.25	0.52	0.32
sabinene	0.03-0.05	0.10	0.07	neryl formate	-	0.01	-
β-pinene	0.10-0.20	0.20	0.14	geranyl formate	-	0.02	-
myrcene	0.25-0.40	0.10	0.22	methyl (E)-geranate	0.05-0.10	0.06	0.02
α-terpinene	0.02-0.03	0.05	0.01	methyl (Z)-geranate	0.02	-	-
p-cymene	0.01-0.03	0.10	0.01	α-terpinyl acetate	0.05-0.10	0.01	-
limonene	0.05-0.10	0.20	1.28	citronellyl acetate	0.40-0.50	0.94	0.22
(Z)-β-ocimene	0.05-0.10	0.05	-	neryl acetate	0.05-0.10	0.16	0.04
(E)-β-ocimene	0.05-0.10	0.05	0.03	geranyl acetate	0.70-0.80	2.04	0.43
γ-terpinene	0.03-0.05	0.05	0.02	eugenol	1.10-1.20	0.99	1.19
terpinolene	0.05	0.05	0.01	methyl eugenol	1.60-1.70	2.85	0.71
ethanol	1.50-3.00	0.50	1.42	β-damascone	<0.01	<0.01	-
3-methylbutanol	0.05-0.10	0.05	-	β-damascenone	0.015	0.015	+
2-methylbutanol	0.05-0.10	0.05	0.01	α-copaene	0.01-0.05	0.01	-
hexanol	0.10-0.20	0.23	0.12	β-caryophyllene	0.50-0.60	0.54	0.18
heptanol	0.05	0.01	0.09	α-guaiene	0.30-0.40	0.51	0.14
nonanol	0.03	-	0.03	α-humulene	0.25-0.30	0.35	0.10
ethanal	0.01-0.02	-	-	germacrene-D	0.50-0.60	0.97	0.26
pentanal	0.05-0.10	-	-	δ-guaiene	0.50-0.60	0.38	0.10
benzaldehyde	-	0.05	-	aromadendrene	0.10-0.20	-	0.05
heptanal	0.10	0.02	0.04	γ-cadinene	0.05-0.10	0.05	-
octanal	-	0.01	-	δ-cadinene	0.05-0.10	0.05	0.01
nonanal	0.01-0.05	0.05	0.04	elemol	0.10-0.20	-	-
decanal	0.03	-	0.03	valerianol	0.05-0.10	-	-
rosefuran	0.02	0.02	0.01	α-cadinol	0.05-0.10	-	-
cis-rose oxide	0.20-0.30	0.36	0.09	δ-cadinol	-	0.01	-
trans-rose oxide	0.10-0.15	0.19	0.04	β-eudesmol	0.20-0.40	0.15	-
nerol oxide	0.05-0.10	0.05	0.03	δ-guaiol	0.01-0.02	-	0.01
linalool	2.10-2.30	0.81	0.11	(E,Z)-farnesol	1.40-1.50	1.38	0.11
2-phenylethanol	1.70-2.00	1.85	67.53	tetradecane	0.05-0.10	-	-
terpinen-4-ol	0.20-0.30	0.46	0.02	pentadecane	0.50-0.60	-	0.26
α-terpineol	0.60-0.80	0.25	-	hexadeca(e)nes	0.02	-	0.22
γ-terpineol	0.05-0.10	-	-	heptadeca(e)nes	1.50-1.70	-	0.84
myrtenol	-	0.04	-	octadeca(e)nes	0.35	0.05	0.17
myrtenal	-	0.01	-	nonadeca(e)nes	14.00-15.00	3.05	3.85
α-citronellal	-	0.01	-	cosa(e)nes	1.30-1.50	0.11	0.29
citronellal	-	0.06	-	hencosa(e)nes	4.00-5.00	0.10	0.78
α-citronellol	0.10	-	-	docosa(e)nes	0.30	0.02	0.09
citronellol	27.50-28.00	45.00	7.77	tricosa(e)nes	1.00-1.20	-	0.23
nerol	7.80-8.60	10.10	2.15	tetracosa(e)nes	0.05-0.10	-	0.07
carveol	0.05-0.10	0.14	0.02	pentaeicos(e)nes	0.50	-	0.11
neral	0.50-0.70	0.82	0.19	hexacosane	0.50	-	0.72
geraniol	16.00-17.00	20.50	4.15	ethyl palmitate	0.05	-	0.02
geranial	0.50-1.00	1.34	0.33	2-phenethyl laurate	0.06	-	-

- = absent; + = present

CO_2-extracted rose oil is only about one third the value of the hydrodistilled oil.

We carried out an intensity comparison test between the hydrodistilled rose oil and the CO_2-extracted oil. The oils were presented in 0.5, 0.75 and 1% solutions to 22 observers in all possible paired combinations. Figure 1 shows the intensity score plotted against the logarithm of the concentration. It was found that the hydrodistilled rose oil was about two to three times more odor-intensive than the CO_2-extracted oil.

Conclusion

The odor intensity of the CO_2-extracted bitter orange oil was twice that of the hydrodistilled oil, because more odor-intense constituents are extracted with CO_2 and fewer compounds decompose during the extraction than in boiling water during hydrodistillation. Just the reverse is true for the two rose oils with respect to the odor intensity, due to the fact that much (65%) of the less odor-intense 2-phenylethanol is dissolved in the distillate water and therefore is not present in the hydrodistilled oils.

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Table IV. Concentrations of main constituents, threshold values and odor units of Bulgarian rose oils

Compound	Concentration hydro-distilled (%)	Concentration CO_2 extract (%)	Threshold value in water (ppb)	Odor units x 10^{-3} hydro-distilled	Odor units x 10^{-3} CO_2 extract
citronellol	30	8	40	7,500	2,000
geraniol	18	4	75	2,400	530
nerol	9	2	300	300	67
linalool	2	0.1	6	3,300	165
2-phenylethanol	2	67.5	750	25	900
rose oxides	0.5	0.15	0.5	10,000	3,000
nerol oxide	0.05	0.03	0.5	1,000	600
eugenol	1	1	30	330	330
methyl eugenol	2	0.7	820	25	10
farnesol	1.5	0.1	20	750	50
β-damascenone	0.015	<0.005	0.01	15,000	<5,000
Total odor units				**40,630**	**<12,652**